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Synthesis and Structure of 1,2,3 Superconductors with Alkaline-earth Ions

G. NARDIN, L. RANDACCIO and E. ZANGRANDO

Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste (Italy)

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Since the discovery by Bednorz and Muller [1] that $La_{2-x}CuO_4$ cuprates have a superconducting transition in the 15–40 K region, a rapid advance has occurred in the last 2 years. In fact, mixed oxides such as $YBa_2Cu_3O_{7-x}$, the so-called 1,2,3 superconductors, have been shown to become superconductors at temperatures up to 90 K [2]. Although, more recently, new mixed cuprates of formula $M_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (with n = 1–3 and M = Bi and Tl) having a critical temperature, T_c, up to 120 K have been reported and structurally characterized [3], the 1,2,3 superconductors still remain the most widely studied. Structural investigations have established that these mixed oxides crystallize with an oxide-defective structure strictly related to that of perovskite. Tetragonal ($x < 0.5$) [4] and orthorhombic ($x > 0.5$) [5] crystal structures were found as a function of the oxide content (Fig. 1). Superconductivity is exhibited only by the orthorhombic forms [5].

Preliminary studies of the influence of substitution of Y by lanthanide cations [6] and of Ba^{2+} ions by Sr^{2+} and Ca^{2+} [7] on the properties and the crystal structure of 1,2,3-type compounds have been carried out. These results indicate that complete substitution of Y by lanthanides (except for Pr and probably Ce and La [8]) does not affect substantially the superconducting properties of the resulting cuprates. On the other hand, the complete replacement of Ba with either Sr or Ca causes the loss of superconductivity of the resulting products. However, it has been claimed that compounds $YBa(AE)Cu_3O_{7-x}$ (AE = Ca or Sr) and $YCaSrCu_3O_{7-x}$ are superconductors with a T_c not far from that of the parent compound [7].

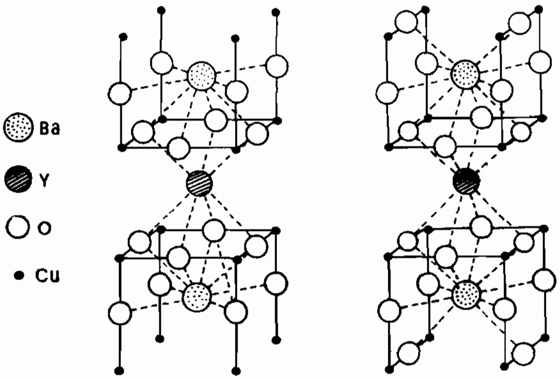

Fig. 1. Tetragonal (x = 1) and orthorhombic (x = 0.5) unit of the $YBa_2Cu_3O_{7-x}$ cuprates.

In order to obtain further insight into the influence of Ba and Y replacement on the properties and structures of 1,2,3 superconductors, we have undertaken a systematic study concerning the synthesis and structural characterization of mixed oxides where Ba and Y are replaced by other alkaline-earth and lanthanide-metal ions, respectively. Preliminary results on the replacement of Ba, differing in part from those previously reported [7], are described.

Powders of mixed oxides with the starting composition corresponding to the appropriate ratio of metal ions were treated following the usual procedures [7]. The composition is indicated by the chemical formulas reported below. Typical X-ray powder spectra are reported in Fig. 2. Their comparison shows that only the $YBaSrCu_3O_{7-x}$ compound has the characteristic powder spectrum of 1,2,3 superconductors, suggesting that this oxide has a structure very similar to that of the parent compound, but with a slightly smaller unit cell. In fact, tetragonal cell parameters derived from the X-ray powder spectrum of Fig. 2d are $a = b = 3.825(3)$ and $c = 11.475(5)$ Å for the tetragonal system. These figures should be compared with those of the tetragonal form of the parent compound [4] which are $a = b = 3.8639(6)$ and $c = 11.849(2)$ Å, and with those of the orthorhombic one [5] which are $a = 3.8282(4)$, $b = 3.8897(4)$ and $c = 11.640(2)$ Å. Using the unit cell parameters experimentally derived above, the X-ray powder spectrum of this species, calculated assuming the coordinates of the parent compound in the *P*4/*mmm* space group and that half of the Ba is replaced by Sr, agrees well with the experimental one, as shown in Fig. 2. This structure is still maintained for Ba/Sr ratios up to 1/3. When Ba is completely replaced by Sr, a multiphase system with composition strongly dependent on the reaction conditions is obtained. A typical X-ray powder spectrum for $YSr_2Cu_3O_{7-x}$ is reported in Fig. 2. On the other hand, the spectrum analysis suggests that $YCaSrCu_3O_{7-x}$ has the same structure as $YCa_2Cu_3O_{7-x}$, while the preparation of $YBaCaCu_3O_{7-x}$ species results in a mixture of two compounds, $YCa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$, since its powder spectrum is the sum of the two latter species.

Resistivity measurements indicate that $YBaSrCu_3O_{7-x}$ is a superconductor with $T_c \approx 70$ K (Fig. 3a). Superconductivity is also exhibited by the mixture of $YCa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$ oxides (Fig. 3b) and should be attributed to the presence

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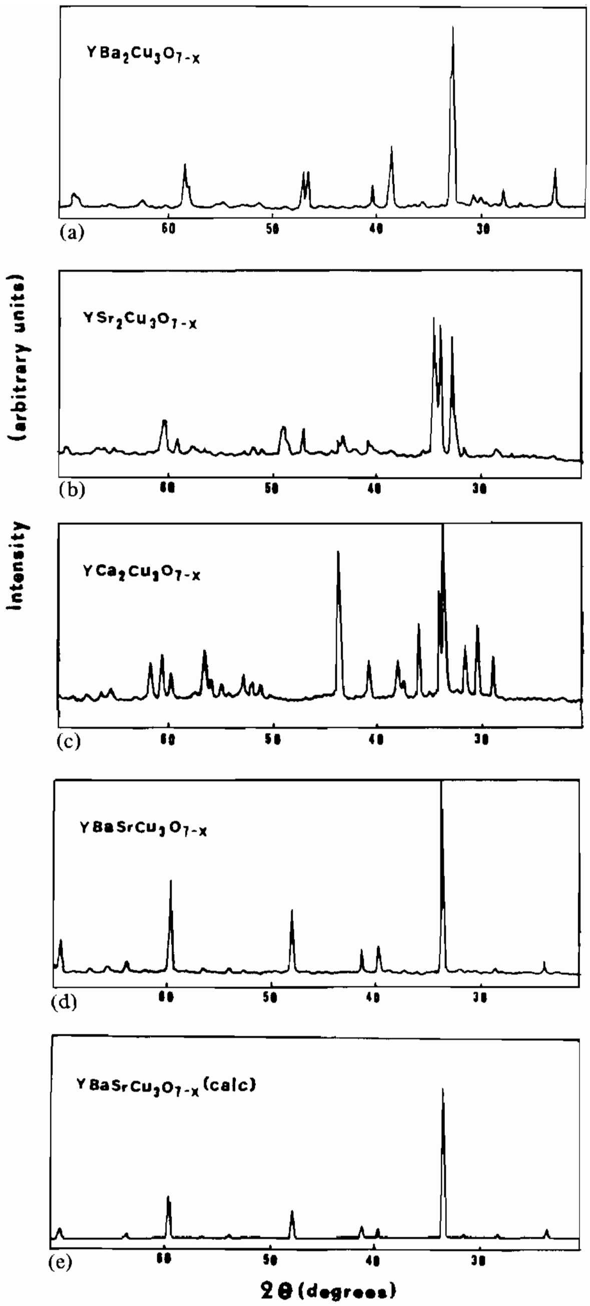

Fig. 2. X-ray powder spectra of $YM_2Cu_3O_{7-x}$ when (a) M = Ba; (b) Sr; and (c) Ca. Observed and calculated X-ray powder spectra for $YBaSrCu_3O_{7-x}$ are represented in (d) and (e), respectively. Intensity I is on an arbitrary scale.

of about 50% of the latter oxide in the mixture. On the contrary, all the samples of $YCaSrCu_3O_{7-x}$ we have prepared do not show superconductivity, in contrast with the previous report [7], as they are semiconductors. All the above results suggest that the 1,2,3 structure is strongly influenced by the size of the alkaline-earth cation. Thus, Ca^{2+} ions,

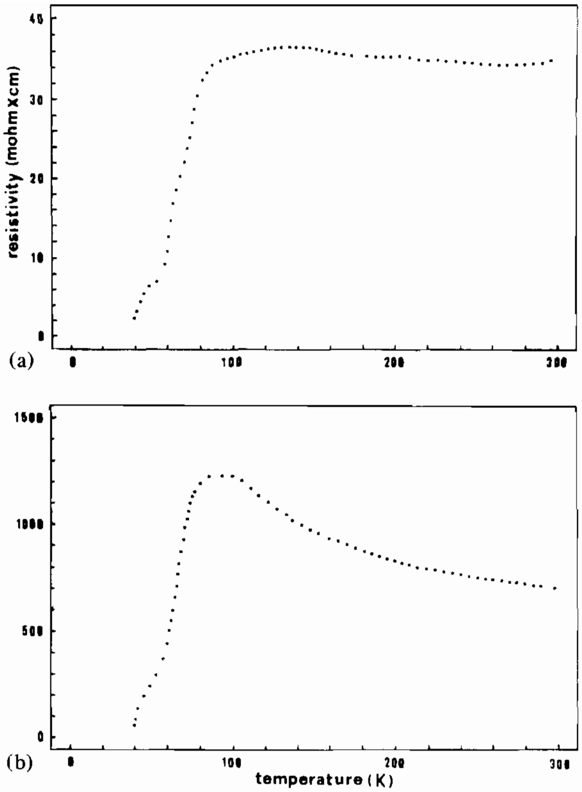

Fig. 3. Resitivity *vs.* temperature for (a) $YBaSrCu_3O_{7-x}$ and (b) for the preparation with starting composition $YBaCaCu_3O_{7-x}$.

having a radius of 0.99 Å, are too small to *properly* substitute Ba^{2+} ions which have a radius of 1.35 Å. On the other hand, Sr^{2+} ions, with a radius of 1.13 Å, can partially replace both Ca^{2+} and Ba^{2+} in their respective structures without a strong destabilizing effect. It should be noted that in all the crystal structures of superconductors so far determined the barium site has never been found to be occupied by calcium.

Attempts are being made to characterize the species with starting composition $YCa_2Cu_3O_{7-x}$.

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